

Attorney Docket No. 5002.02-1  
Customer No. 23308

### **REMARKS/ARGUMENTS**

The Office Action dated 12/13/2005 rejected claims 1-11 and 24-28; No claims were allowed. Claims 12-23 were cancelled by preliminary amendment pursuant to an earlier restriction requirement. By this Amendment, claims 1, 3 and 24 are amended. Claim 8 is amended to correct a dependency.

Turning now to the Detailed Action, the following remarks are set forth and responded to in the same order as presented in the Office Action.

#### **1. Information Disclosure Statement**

The Yin et al. publication was not considered because a copy of it was assertedly not supplied in the parent case.

#### **Response**

A copy of the Yin et al. publication was submitted with the amendment submitted in the parent case on September 11, 2003. This publication was provided to show differences between films deposited by electroless deposition and by vapor deposition, and is referred to in the immediately subsequent Office Action of 11/24/03. Pursuant to MPEP 609.02, consideration of this publication and its listing on the patent is respectfully requested.

#### **2. Claim Objections**

Claim 3 was objected to for incorrect grammar.

#### **Response**

This grammar has been corrected.

#### **3. Rejection of Claims 1, 2, and 5-11 under 35 USC §102(b) over Calvert et al.**

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The Office Action states that Calvert et al. discloses a method for forming a diffusion barrier according to the steps of claim 1 (now amended) and further discloses the uses of different molecules recited in claims 2, 6, and 7-11. Calvert et al. is also said to disclose the heating step of claim 5.

### **Response**

Claim 1 has been amended to recite depositing the metal layer on the diffusion barrier by vapor depositing copper onto the self-assembled monolayer, whereby said barrier layer inhibits copper diffusion into the substrate.

Support for this amendment may be found in the specification at page 7, para [31], para [33] (inhibits diffusion of copper) and in example 1, paragraph [37] in particular. Literal support for the phrase of “vapor deposition” may be found in original claim 24.

Claim 1 as presently amended is neither anticipated nor rendered obvious by Calvert et al.

**First, Calvert et al. do not disclose a method of forming a device having a diffusion barrier,** as presently recited in claim 1. The words “diffusion” and “barrier” do not appear in this reference and there is no discussion of either feature. Instead, Calvert et al. disclose a process for electroless metallization. Electroless metallization involves the application of a catalyst to a substrate followed by immersion of the complex in a solution containing metal, whereby the catalyst causes the metal to be deposited on the substrate in regions where the catalyst is located. As stated in the Abstract,

“In one aspect, the invention is characterized by the use of chemical groups capable of ligating with an electroless metallization catalyst, including use of ligating groups that are chemically bound to the substrate. In a preferred aspect, the invention provides a means for selective metallization without the use of a conventional photoresist patterning sequence, enabling fabrication of high resolution metal patterns in a direct and convenient manner.”

There is no teaching or suggestion that the adhesive layer used to bind the catalyst serves as a barrier layer. The adhesive layer may not be said to inherently serve such a

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purpose in any disclosed embodiment.

**Second, Calvert et al. do not suggest the recited combination of  $\beta$ -trimethoxysilylethyl-2-pyridine with copper.** This applies to claims which read on the use of this compound, namely, 1, 2, 4, 5, 7, 8, and 11. As to these claims, Calvert et al. do not disclose the use of copper.

The adhesive layer of Calvert et al. may be “a variety” of materials that provides ligating and adhesive properties (Col. 4, l. 10). The disclosed adhesive film is in most cases composed of a different material than that recited in the present claims. Namely, the adhesive layer is in most examples is “UTF-14B3,” which is formed from a mixture of a bipyridine and a propylamine (See Col. 14, l. 35). In examples (e.g., 1-3, 11, 12, 19-21, 22) using  $\beta$ -trimethoxysilylethyl-2-pyridine, the metal used was not copper, but rather cobalt or nickel (example 24).

Furthermore, as shown in Examples 21 and 23 of the reference, the UTF-14B3 is said to be superior for purposes of the disclosed process than the  $\beta$ -trimethoxysilylethyl-2-pyridine. Thus, there is no suggestion to modify the process using  $\beta$ -trimethoxysilylethyl-2-pyridine to a process using copper.

**Third, Calvert et al. do not teach a process comprising the step of “forming a metal layer on the diffusion barrier as formed in step (c) using a vapor deposition process.”** Electroless plating and sputtering are two completely different methods. In electroless plating, an adhesive film may be used to attach catalyst in desired regions of metal deposition; however, no analogous procedure exists in a vapor deposition process (e.g., sputtering). Electroless plating typically needs a seed layer which facilitates the metal deposition. Vapor deposition does not. Furthermore, in the patterning step as disclosed in the references, the adhesive film is modified prior to metallization, unlike the presently claimed process, which recites “depositing the metal layer on the diffusion barrier as formed in step (c). . . .”

Furthermore, the two processes yield copper layers with different properties, as shown by the Yin reference, enclosed.

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The two different processes are each key components of the presently claimed invention and the references. Modification of this step would render the processes of the references inoperable.

Accordingly, it is believed that claims 1 (amended), 2 and 5-11 are patentable over the cited reference and withdrawal of this rejection is respectfully requested.

**4. Rejection of Claims 1, 3 and 4 under 35 USC §102(b) over Schnur et al. US 5,079,600**

Schnur et al. is said to disclose a method for forming a diffusion barrier layer comprising the steps of preparing the silicon substrate, contacting the substrate with a composition comprising self-assembling monolayer subunits and a solvent, and removing the solvent.

**Response**

Claim 1 has been amended to recite that the process includes the step of “forming a metal layer on the diffusion barrier as formed in step (c) using a vapor deposition process.” Therefore, as acknowledged in the Office Action, rejection under 35 USC §102 is no longer appropriate. Schnur et al. is discussed in detail below in connection with the rejection of claim 24 et seq. under 35 USC §103. All arguments set forth below in connection with claim 24 are applicable to a possible rejection of claim 1 under 35 USC §103 as well.

Accordingly, it is believed that claims 1 (amended), 3 and 4 are patentable over the cited reference and withdrawal of this rejection is respectfully requested.

**5. Rejection of claims 24-30 under 35 USC § 103(a) over Schnur et al. in view of ASM Handbook and Porterfield**

—The Office Action states as follows:

"Schnur et al. discloses a method of forming a device, the method comprising: providing a substrate [see Fig. 1A]; **providing a diffusion barrier layer (called "thin film")**, wherein the diffusion barrier comprises a self-assembled monolayer [see col. 10, lines 42-47], wherein the self-assembled monolayer is a single layer of molecules [see col. 7, lines 11-15], and wherein the molecules in the self-assembled monolayer have first ends attached to the substrate and second ends projecting upward from the substrate [see Fig. 1A]; and **forming a metal layer on the diffusion barrier layer using a vapor deposition process**, wherein the metal layer is in direct contact with the second ends of the molecules in the self-assembled monolayer [see col. 9, lines 10-17], wherein a seed layer of Pd/Sn is coated over the self-assembled monolayer; see col. 4, lines 14-17, wherein vapor deposition is given as a known method for fabricating metal paths; and see Fig. 3A for the configuration thereof].

**Schnur et al. does not disclose that the metal layer is copper.** The ASM Handbook teaches that copper may be used as a catalyst for electroless plating of copper (pp. 315-318, especially p. 318, sections entitled "Catalyzation" and "Copper catalyst"). Regarding claim 25, it is held absent evidence to the contrary that the diffusion barrier of Schnur et al. is capable of preventing diffusion of metal atoms from the metal layer into the substrate when the semiconductor device is exposed to an electric field of 2 J1V / cm at about 2000 for about 30 minutes. Basis for this reasoning is that Applicant is using the **exact same self-assembling monolayer as is Schnur et al. to form the barrier layer. Schnur et al. also points out in Example 24 that copper diffusion does not occur even under the stress of an electric field.**

## Response

### 1. Schnur disclosure

As stated in their Abstract, Schnur et al. teach the use of a self-assembling film that is chemically absorbed on the substrate's surface. The chemical reactivity in regions of the ultra-thin film is altered to produce a desired pattern in the film. A catalytic precursor, which adheres only to those regions of the film having enough reactivity to bind the catalyst, is applied to the film's surface. The catalyst coated structure is then **immersed in an electroless plating bath** where metal plates onto the regions **activated by the catalyst.**

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As stated at Col. 10, 1.67 of the reference,

**“by irradiating selected regions of the silane monolayer with UV light, in the manner indicated in FIG. 2, the reactive moieties at the irradiated silane molecule undergo photo-induced cleavage. When the Pd/Sn colloidal catalyst, as schematically indicated in FIG. 3A and 5B, is spread over the surface of the wafer, the colloidal catalyst binds only to the moieties at the interface that it is adherent to. The catalyst does not adhere to the groups whose reactive moieties were inactivated by exposure to the radiation or moieties such as UTF4 (1,1,1,3,3,3-hexamethyldisilazane) to which the colloid does not adhere well.”**

In Example 24,

**“Fabrication of MOS capacitor test structures, an n-type silicon wafer with a 100 nm thick thermal oxide layer was cleaned and treated with UTF3 (4-aminobutyldimethylmethoxysilane) as in example 14. The film was patterned using a mask with standard capacitor test structures and irradiated for 28 minutes with an Hg/Ar lamp. The wafer was metallized with the standard copper plating procedures, used in Example 5, yielding metal squares 800 microns on a side (area=6.times.10.sup.-3 cm.sup.2) The metal/thermal oxide/n-type silicon (MOS) capacitors were then characterized by probing the metal pads and the back of the wafer with a Micromanipulator automatic C-V measuring system. The capacitance was found to be 26 pF/cm<sup>2</sup> with minimal (10 mV) hysteresis and remained stable at room temperature for at over 3 weeks, indicating that device degradation due to masked metal contamination (diffusion of copper into the thermal oxide) was not a problem.”**

## **2. Claim differences**

**(A.) Schnur et al. teach a method for electroless plating, while the claimed methods utilize vapor deposition.**

Claim 24 recites “forming a metal layer comprising copper on the diffusion barrier layer as formed in step (b) using a **vapor deposition process**,” whereas Schnur et al. and the other references cited teach an **electroless plating process**. These are completely different processes. There is no suggestion in the art to modify the process of Schnur et al.

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to employ a vapor deposition of the copper layer, since a key feature of Schnur et al. is to provide a catalytic precursor which is altered to control electroless plating.

**(B) The process of Schnur et al. involves modification of the as-formed SAM.**

Furthermore, claim 24 recites “forming a metal layer comprising copper on the diffusion barrier layer as formed in step (b),” Schnur et al. teaches modification of their self-assembling film to selectively increase or decrease catalyst binding. This modification involves removal or chemical alteration of a “terminal moiety” as shown in Figs. 2 and 3.

**(C) The devices produced by the methods of Schnur et al. and the devices produced by the recited methods are not inherently equivalent.**

It is also asserted that the presently recited diffusion barrier layer is “inherently” found in Schnur, because Applicants are using “the exact same self-assembling monolayer as is Schnur,” and because Example 24 allegedly discloses barrier properties.

**(i) Method claims versus structures**

First, since the claims now are directed to a method of forming a device comprising the step of forming a metal layer on the diffusion barrier using vapor deposition, and further applying the metal layer to the diffusion barrier formed in the preceding step, there are process limitations in the present claims that are not taught or suggested by Schnur et al., regardless of the alleged identity of the self-assembled monolayer. As stated above, the methods of Schnur et al. cannot be used with vapor deposition and require that the self assembled monolayer be treated to selectively absorb catalyst at specific locations, and, of course, require the addition of catalyst prior to addition of the metal.

**(ii) Inherency of diffusion barrier**

Schnur et al. Example 24 teaches the use of 4-aminobutyldimethylmethoxysilane (UTF3). This compound is not embraced by claims 2 (where each “Y” is an O-alkyl group), or claim 3, wherein each Y is a halogen, or claims 6-11. These claims are therefore clearly

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unobvious over the cited combination. Also, there is no motivation to use copper as a catalyst in the present process, which uses no catalyst, and furthermore is directed to preventing diffusion of copper.

As to claims 1 and 24, it is submitted that the monolayer of Example 24 cannot inherently possess the recited barrier property. The single sentence stating that diffusion “was not a problem” suggests only that the adhesion treatment did not make diffusion worse.

**The test done in Example 24 does not indicate any practical barrier property.**

It has been shown since that C-V hysteresis alone (in the absence of other corroborating measurements such as leakage current, TVS etc.) is insufficient to claim lack of Cu contamination. Kizil et al., “TiN, TaN, and W<sub>x</sub>N as diffusion barriers for Cu on SiO<sub>2</sub>: Capacitance-voltage, leakage current and triangular-voltage sweep tests after bias temperature stress,” Thin Solid Films, 449:158-165 (2004) is included herewith as indicative of the state of the art of testing diffusion barriers. It is clear that various tests are important, and are conducted under conditions of bias thermal stress (BTS). BTS was not used in Schnur et al. The room temperature test disclosed in Schnur et al. is not an adequate measure of diffusion barrier properties, even if one assumes that interpretation of the sentence in Example 24. Copper diffusion without electric fields occurs only above 100°C (for extended times) or 500-600°C for shorter times –in both cases without electric fields.

Accordingly, it is believed that method claims 24 (amended) and 25-28 are patentable over the cited references and withdrawal of this rejection is respectfully requested.

### **CONCLUSION**

Applicants request that the rejections of claims 1-11 and 24-28 be withdrawn for the reasons advanced above. It is believed that the present Amendment is fully responsive to the presently outstanding Office Action and should place the application in condition for



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allowance. Reconsideration and allowance of currently pending claims 1-11 and 24-28, as well as the timely issuance of a Notice of Allowance is earnestly solicited. The Examiner is respectfully invited to call the undersigned at the number below if the prosecution of the subject application may be expedited by a telephone conference.

Respectfully submitted,

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